Atmospheric pressure Ar / CF_4 plasma jet and surface modification on epoxy resin

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Abstract: In this paper, atmospheric pressure plasma jet is generated in a quartz tube and the working gas is the mixture of Ar and CF_4. Comparing to working gas of pure Ar, after adding CF_4 to Ar gas as the working gas, the length of the plasma becomes shorter and the colour of plasma turns from purple to yellow. After treated by APPJ, the water contact angle of EP decreases, which means the hydrophilia of EP increases. Comparing to pure Ar, after adding CF_4 to the working gas, the hydrophobicity of EP increases relatively. The spectrum chart shows the increase of CF_3 radicals as we increase the concentration of CF_4 to the working gas.

Keywords: epoxy resin, atmosphere pressure plasma jet, surface modification, hydrophilia

1. Introduction

Atmosphere pressure plasma jet (APPJ) has attracted considerable attention due to its potential use in many applications such as biomedicine[1] and material treatment[2-4]. Atmospheric plasma jet can be generated directly in the atmosphere and is less restricted by the surrounding environment. What's more, atmospheric plasma jet can handle irregular surface materials, and it is easy to realize large-scale processing. The processing distances of electrons, ions and active components in the plasma jet can be up to 5cm-10cm[5]. Therefore, APPJ is widely used for film deposition and surface etching of materials. Finally, due to the difference of the working gas, the active particles contained in the atmospheric plasma jet will also change[6]. Therefore, the selection of different types, or different concentrations of the same type of working gas to treat the material, the material surface will have different treatment effect.

Epoxy resin (EP) is the general name of a kind of polymer containing more than two epoxy groups in molecules. Due to the good electrical properties of epoxy resin materials, it is widely used as an insulating material in electrical equipment. In order to enhance the electrical properties of EP surfaces, many researchers use APPJ to modify the EP surface. Alexey Kondyurin and Marcela Bilek[7] observed the structural changes and etching processes, associated with argon plasma and plasma immersion ion implantation treatment in uncured epoxy resin coatings . The process of structure degradation is observed to be independent of the functionality and size of the chemical group being degraded. Shao Tao et al[8] investigated the effects of surface charge on DC surface flashover characteristics for original and treated EP by APPJ. They discovered that with the increase of the plasma treatment time, the peak value of surface charge in the center of the samples decreases.

One of the effective methods for surface modification of materials is plasma treatment[9,10], and the plasma with CF_4 as working gas has received close attention due to its mild etching effect and strong fluorination characteristics[11,12]. In order to investigate the effect of surface modification by APPJ and the influence of different content of CF_4 in the working gas. In this study, Ar/CF_4 were used as the working gas to generate the APPJ and treat the surface of EP. The flow rate of Ar was maintained while the content of CF_4 was changed from 0 to 80sccm (standard cubic centimeter per minute).

2. Experimental Setup

The EP used in the study is 3240 epoxy resin and the thickness of it is 1mm. The schematic of the experiment is shown in Fig. 1. The APPJ is driven by the high voltage pulsed generator (HV-2015, Xi'an Lingfeng Co., Xi'an) with frequency from 1 Hz to 100 kHz and voltage from 0 to 20kV. In this study, the frequency is 10 kHz and voltage is 3.2 kV. The Ar and CF_4 gas was controlled by the flow meter (DSN-100, Dexin Technology Electronics Co., Dongguan) and the maximum flow rate is 5slm (standard litre per minute). The Ar (purity:99.999%) and CF_4 (purity:99.999%) gas flows through the quartz tube. In this experiment, the flow rate of Ar gas is always maintained at 3slm, while the content of CF_4 is not fixed. The treating time of each group of experiments is 40 s. In order to exhaust the air in the quartz tube, the working gas was injected for 1min before the experiment to ensure the purity of the working gas.

The plasma generator used in this paper is a needle ring structure based on DBD principle. The needle electrode is connected with the positive electrode of high-frequency pulse voltage and the other end is inserted into the quartz tube.The ring electrode is wrapped outside the quartz tube.The inner radius of the tube is 4 mm and the outer radius is 5 mm, The thickness of the ring is 6mm, the ring is 5mm from the inner tip of the pipe and 2 mm from the nozzle. The ring electrode is grounded.

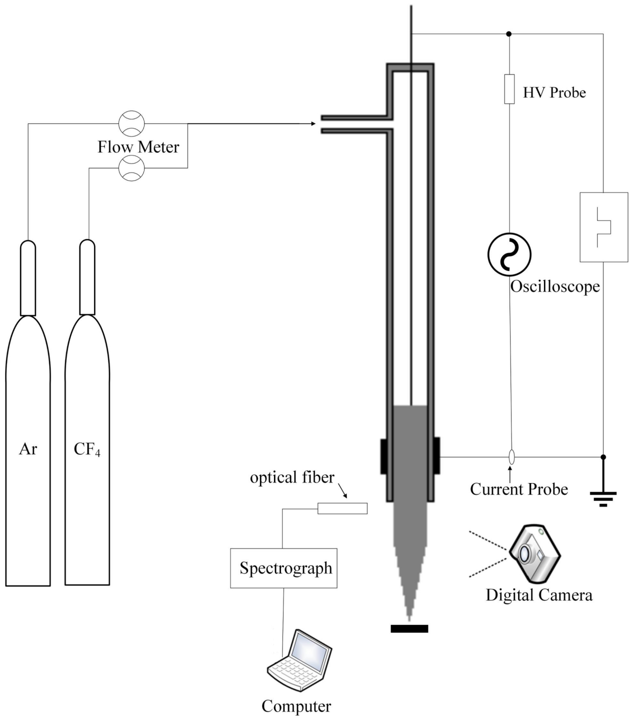


Fig. 1. Schematic diagram of APPJ experimental device.

The four-channel oscilloscope (Tektronix MDO 3034) was used to record the waveform of voltage and current, which has a real-time sampling of 5 Gs/s and bandwidth is 1 GHz. The high-voltage probe (Tektronix P6051A) was used to measure the voltage waveform while the current probe (Pearson 2877) was used to measure the current. Water contact angle tester (JGW-360A, Chenghui, Shandong, China) was used to test the static water contact angle. The spectrum is recorded by spectrometer (Ocean-HDX-UV-VIS).

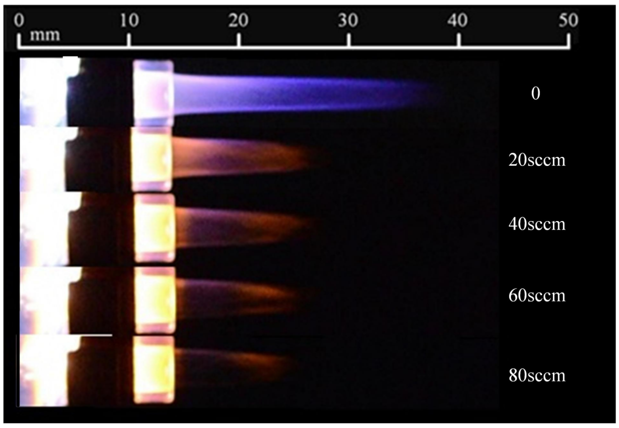
3. Results and Discussion

3.1 Electrical characterization

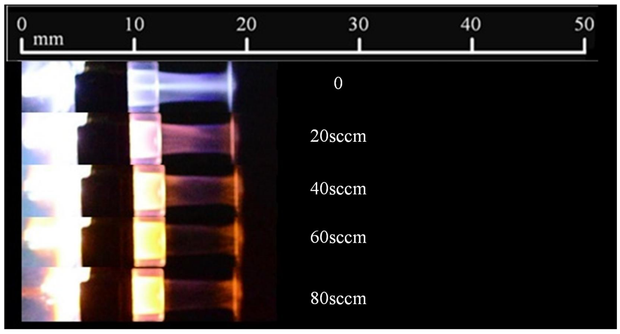
When the applied voltage amplitude is 3.2 kV, the frequency is 10 kHz, the distance between the tube orifice and EP surface is 7 mm and Ar gas velocity is fixed at 3 L/min, The discharge image of atmospheric pressure Ar plasma jet is displayed in Fig. 2. The colour of the Ar plasma is purple because the influence of excited Ar species. the length of the jet is about 38 mm. After adding CF4 into the plasma, The colour of the plasma turn to yellow and the length of the jet becomes shorter. The colour of the plasma changes because after adding CF4, There are species containing the F element in the plasma. As the content of CF4 increases, the colour of plasma jet gradually develops from purple to yellow, and the length of plasma jet gradually decreases. The shape of the plasma is stable because the mode of discharge is glow discharge at 3.2 kV.

The voltage waveform and current waveform of APPJ discharge are shown in Fig. 3. From the picture we can see that in the rising edge of the voltage there is a positive current peak in the falling edge there is a negative current peak. Because of the high frequency, the applied voltage can be considered as a constant.

In the case of pure Ar, the value of the positive peak of current is 364 mA and the negative current peak is 268mA. After adding CF_4, the current changed slightly.After adding 20sccm CF_4 in 3slm Ar, The value of the positive peak of current is 476 mA and the negative current peak is 356mA. After adding 40sccm CF4 in 3slm Ar, The value of the positive peak of current is 500 mA and the negative current peak is 508mA.After adding 60sccm CF_4 in 3slm Ar, The value of the positive peak of current is 492 mA and the negative current peak is 340mA.After adding 80sccm CF_4 in 3slm Ar, The value of the positive peak of current is 404 mA and the negative current peak is 380 mA. After adding CF_4, the current of plasma increases about 100-150 mA.



(a)



(b)

Fig. 2. The change of APPJ at different content of CF4.

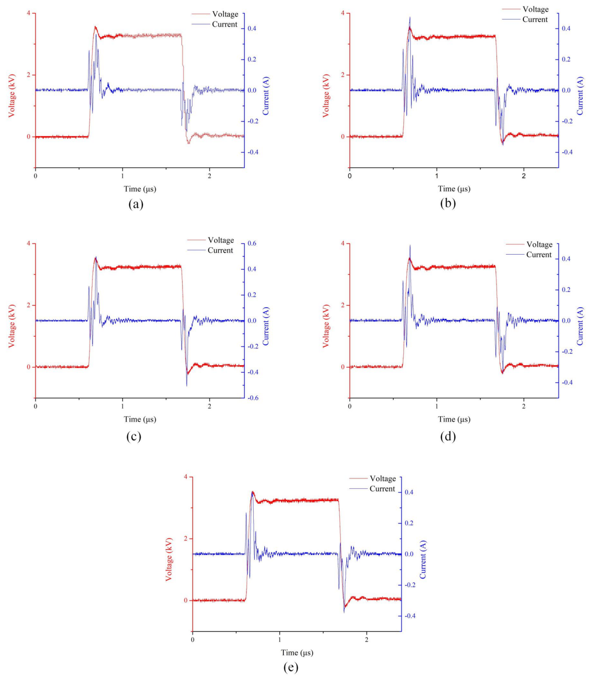


Fig. 3. Comparison of the I−V characteristics of He APPJ at different content of CF_4. (a) pure Ar, (b) Ar+20sccm CF_4, (c) Ar+40sccm CF_4, (d) Ar+60sccm CF_4, (e) Ar+80sccm CF_4.

3.2 Water contact angle

The water contact angle of untreated EP is 71.58°. Five groups of experiments were carried out under different working gas: (a) 3slm Ar; (b) 3slm Ar+20sccm CF_4; (c) 3slm Ar+40sccm CF_4; (d) 3slm Ar+60sccm CF_4; (e) 3slm Ar+80sccm CF_4. Each set of experiments was repeated 10 times and get the average value of the water contact angle. From Fig. 4, after treated by APPJ of pure Ar, the water contact angle changes to 32.47°. The hydrophilia of the EP surface increase a lot. When we added CF4 into Ar as the working gas, the water contact angle changed. Comparing to pure Ar, after adding 20sccm CF4, the water contact angle increases to 55.79°. After adding 40sccm CF_4, the water contact angle increases to 57.68°. After adding 60sccm CF_4, the water contact angle stopped increasing and decrease to 54.19°. After adding 80sccm CF_4, the water contact angle maintain in 54.61°.

After treated by the plasma, the water contact angle of EP surface decreased. There are two reasons for this phenomenon: for one thing, the Ar plasma is consist of many energetic particles. EP is etched by the plasma and the surface of EP becomes more rough. According to the theory of Wenzel,[13] when the contact Angle is less than 90°, increasing roughness of EP surface results in smaller contact Angle. Secondly, the atmospheric pressure Ar

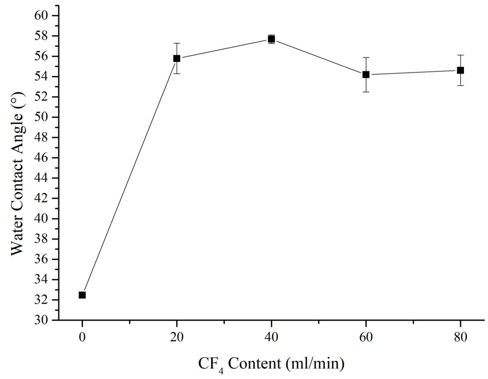


Fig. 4. Water contact angle of EP after treated by APPJ of different concentration of CF_4.

plasma contains many active oxygen groups, which are highly hydrophilia groups. Comparing to pure Ar, after adding CF_4, the water contact angle increase significantly. The reason for this phenomenon is that after mixing CF_4 as working gas, there were active groups associated with fluorine, which are hydrophobic groups. These groups attached to the surface of the material so after adding CF_4, the water contact angle relatively increased. These will be confirmed by the subsequent results.

The water contact Angle generally increases because when the treated material is placed in the air, its surface properties will degrade to some extent, which is called "aging effect"[14]. Except in the case of 20sccm CF_4, The water contact angle recovers significantly because the treatment time of our experiment is short and the surface composition is not particularly stable.

3.3 Spectral characterization

The spectrum of Ar+CF_4 APPJ at different content of CF4 is shown in Fig. 5. The excited species are detected by spectrograph and the optical fiber was placed in the orifice of the quartz tube. The spectrograph detected the excited species of plasma plume. In our study, we mainly discuss the excited species in the plasma plume because it is where the plasma interacts EP surface. The excited species include OH radical (309nm), the second positive system of N_2 (SPS: C3Πu-B3Πg)[15], CF_3 (the center is 614nm)[16] and Ar.

In the case of pure Ar, the intensity of OH radicals peak is about 6.5×10^4 , the intensity of the highest peak of N_2 is about 2.2×10^4 and the intensity of the highest peak of Ar is about 6.2×10^4. After adding CF_4 as working gas, the intensity of OH, N_2 and Ar decrease significantly. As the increase of the CF_4 content, the intensity of OH, N_2 and Ar continue to decline.

4 Conclusion

In this paper, the surface modification on EP by Ar and Ar/CF_4 is studied. Conclusions are as follows:

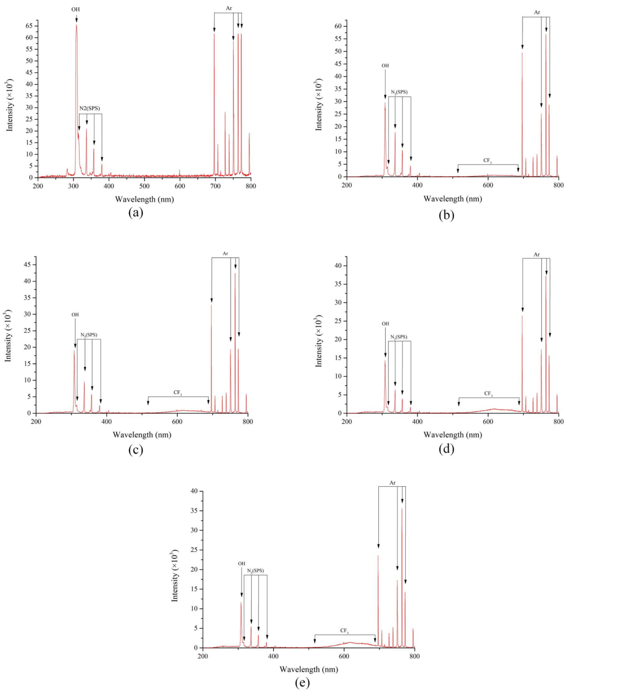


Fig. 5. Comparison of the spectrum of Ar+CF_4 APPJ at different content of CF_4. (a) pure Ar, (b) Ar+20sccm CF_4, (c) Ar+40sccm CF_4, (d) Ar+60sccm CF_4, (e) Ar+80sccm CF_4.

The length and colour of the atmospheric plasma are connected with the composition of the working gas. As we increase the concentration of CF_4 to the working gas. The length of the plasma decreases significantly and the colour of the plasma turns from purple to yellow.

After treated by atmospheric pressure Ar plasma and Ar/CF_4 plasma, the hydrophilia of the EP surface both increase. Comparing to the pure Ar, after adding CF_4 to the working gas, the water contact angle increase relatively.

A large number of excited OH, N_2, CF_3, Ar and other active particles are generated in the discharge process of atmospheric pressure plasma jet. For one thing, EP is etched by these active particles and the surface roughness of EP increased. Secondly, the atmospheric pressure Ar plasma contains many active oxygen groups, which are highly hydrophilia groups. The two reason resulted in the increase of hydrophilia on EP surface. What's more, the water contact angle in the case of Ar/CF_4 relatively increased because of there are many particles in the plasma, which are hydrophobic groups.

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